

Vacancy-driven magnetocaloric effect in Prussian blue analogues

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Abstract

We experimentally show that the magnetocaloric properties of molecule-based Prussian blue analogues can be adjusted by controlling during the synthesis the amount of intrinsic vacancies. For $\text{Cs}_x\text{Ni}_4[\text{Cr}^{\text{III}}(\text{CN})_6]_{(8+x)/3}$, we find indeed that the ferromagnetic phase transition induces significantly large magnetic entropy changes, whose maxima shift from ~ 68 K to ~ 95 K by varying the number of $[\text{Cr}^{\text{III}}(\text{CN})_6]^{3-}$ vacancies, offering an unique tunability of the magnetocaloric effect in this complex.

Key words: Magnetocaloric effect; Prussian blue analogues; Long-range ferromagnetic order

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Magnetic ordering phenomena are efficiently exploited to enhance the magnetocaloric effect (MCE) of magnetic materials [1]. This is possible because the response to the application or removal of magnetic fields is indeed maximized near the ordering temperature. In the search of suitable materials for magneto-cooling applications, however, one may need to adjust the ordering temperature to make optimum use of the magnetocaloric properties of a given material. For conventional materials, such as lanthanide compounds and alloys, it is common practice, in this respect, to partly substitute one constituting element for another one [1]. Here we show that a similar but different strategy can be employed as well in Prussian blue analogues (PBA),

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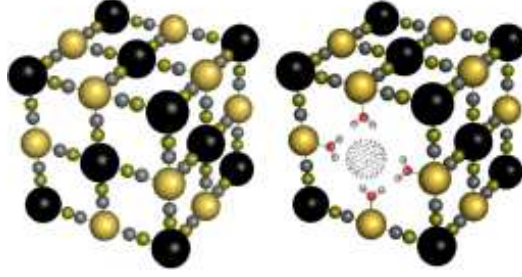


Fig. 1. Sketch of Ni-Cr PBA without any vacancy (left) and with a $[\text{Cr}^{III}(\text{CN})_6]^{3-}$ vacancy, shown as a large bright sphere, coordinated by bound water molecules (right). Black spheres represent Cr^{III} ($S_{\text{Cr}} = 3/2$), whereas lighter-colored spheres represent Ni^{II} (spin $S_{\text{Ni}} = 1$), and small circles denote the cyano-bridge that ensures the exchange coupling between the metallic centers.

which were recently investigated for their magnetocaloric properties [2]. The field of magnetocaloric research on molecule-based materials, such as PBA, is relatively young, although it has already shown promising potentialities [3].

The Prussian blue analogues here reported have the idealized formula $\text{Cs}_x\text{Ni}_4^{II}[\text{Cr}^{III}(\text{CN})_6]_{(8+x)/3}$, and the conventional unit cell is depicted in Fig. 1. Depending on the value of x , the presence of the intrinsic $[\text{Cr}^{III}(\text{CN})_6]^{3-}$ vacancies and their amount per cell is easily seen, as exemplified in the Figure. The non-stoichiometry is known to be essential for the observation of peculiar phenomena in this class of materials, such as photomagnetism for Co-Fe PBA [4]. In what follows, we shall focus on two Ni-Cr PBA having $x = 0$ and $x = 4$, which we shortly denote hereafter as $\text{NiCr}_{2/3}$ and CsNiCr , respectively. The difference between the two resides in the ideally perfect stoichiometry of CsNiCr , for which half of the tetrahedral interstitial sites are occupied by Cs cations which maintain charge neutrality, and in the absence of Cs in $\text{NiCr}_{2/3}$ that results in the presence of vacancies. Both compounds are known to undergo a transition to a long-range ferromagnetic ordered state [5]. Further information on the structure together with a description of the method of synthesis can be found in Ref. [5]. Susceptibility and magnetization measurements were carried out in a commercial apparatus for the $0 < H < 7$ T magnetic field range. All data were collected on powdered samples of the compounds.

For both compounds, Figure 2 shows the complex susceptibility collected with an ac-field $h_{ac} = 10$ G at $f = 1730$ Hz. For CsNiCr , the abrupt change of the in-phase susceptibility $\chi'(T)$ at $T_C \simeq 90$ K is ascribed to the transition to a ferromagnetically ordered state, which is also corroborated by recent specific heat experiments [2]. Figure 2 shows as well that fluctuations in the ordering process gives rise to an out-of-phase susceptibility $\chi''(T)$ signal. The complex susceptibility of $\text{NiCr}_{2/3}$ follows qualitatively that of CsNiCr but at much lower temperatures with a break in $\chi'(T)$ at about 60 K, which is accompanied by a $\chi''(T)$ signal (Fig. 2). The difference between the susceptibilities of the two compounds can be easily explained within the frame of the molecular field

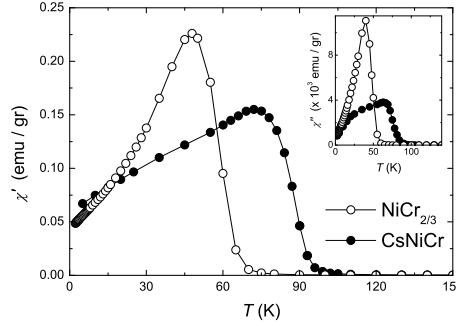


Fig. 2. Complex susceptibility collected at $f = 1730$ Hz and ac-field $h_{ac} = 10$ G, for CsNiCr and NiCr_{2/3}, as labelled. Inset: out-of-phase component $\chi''(T)$.

theory for which the T_C values of the present system can be expressed as

$$T_C = \frac{2(z_{\text{Ni}}z_{\text{Cr}})^{1/2}|J|}{3k_B} \times [S_{\text{Ni}}(S_{\text{Ni}} + 1)S_{\text{Cr}}(S_{\text{Cr}} + 1)]^{1/2} \quad (1)$$

where z_{Ni} and z_{Cr} are the numbers of nearest neighbour metal ions of the Ni^{II} and Cr^{III} ions, respectively, and J is the exchange coupling constant between the Ni^{II} and Cr^{III} ions. The inclusion of [Cr^{III}(CN)₆]³⁻ vacancies accounts for the different T_C 's, since it causes a change in the number of nearest neighbours. It is easy to show, indeed, that although z_{Ni} retains its value by switching from CsNiCr to NiCr_{2/3} (for which $z_{\text{Ni}} = 6$), the z_{Cr} values are 6 and 4 for CsNiCr and NiCr_{2/3}, respectively. Given $S_{\text{Ni}} = 1$, $S_{\text{Cr}} = 2$ and assuming $T_C = 90$ K as for CsNiCr, we obtain from Eq. (1) the exchange coupling whose estimate amounts to $J \simeq 6.5$ K, where the positive sign is set by the ferromagnetic nature of the ordered phase. By switching from CsNiCr to NiCr_{2/3}, it follows, according to Eq. (1), a lower value for T_C that amounts to ~ 60 K for the latter, in good agreement with the susceptibility data (Fig. 2). In Prussian blue analogues, the dependence of T_C on the number of neighbours is well-known, as was already reported for several derivatives including Cs_xNi₄^{II}[Cr^{III}(CN)₆]_{(8+x)/3} as well [5,6,7,8].

For a proper evaluation of the MCE of these compounds [9], we performed systematic magnetization $M(T, H)$ measurements as a function of temperature and field. Field-cooled $M(T, H)$ measurements for several applied-fields H up to 7 T show spontaneous magnetization below the corresponding T_C 's (Fig. 3). In an isothermal process of magnetization, the magnetic entropy change ΔS_m can be derived from Maxwell relations by integrating over the magnetic field

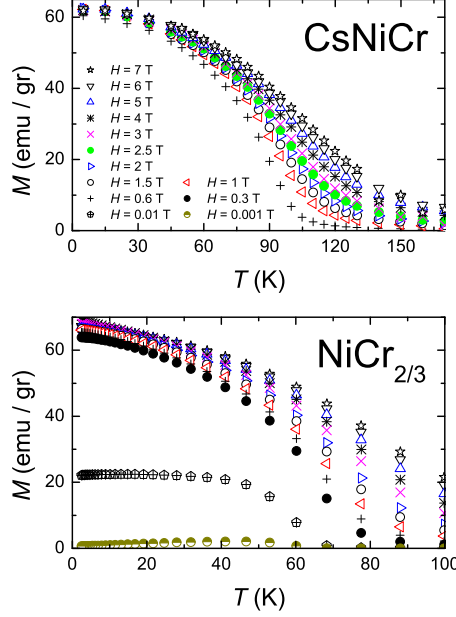


Fig. 3. Field-cooled $M(T)$ curves measured at different applied-fields for CsNiCr (top) and NiCr_{2/3} (bottom), as labelled in the top panel.

change $\Delta H = H_f - H_i$, that is:

$$\Delta S_m(T)_{\Delta H} = \int_{H_i}^{H_f} \frac{\partial M(T, H)}{\partial T} dH. \quad (2)$$

From the $M(H)$ data of Fig. 3, the obtained $\Delta S_m(T)$ for several ΔH values [10] are depicted in Fig. 4. We note that the maximum change of the magnetic entropy upon application of a magnetic field, provides values that are similar for both compounds. Indeed, it can be seen that $-\Delta S_m$ increases by increasing ΔH , reaching for $\Delta H = 7$ T the values of $6.6 \text{ J kg}^{-1}\text{K}^{-1}$ and $6.9 \text{ J kg}^{-1}\text{K}^{-1}$ for CsNiCr and NiCr_{2/3}, respectively. However, since these changes are associated with the mechanism of magnetic ordering [2], it turns out that they take place at well-separated temperatures: ~ 95 K and ~ 68 K, for CsNiCr and NiCr_{2/3}, respectively (Fig. 4). Concluding, the possibility of controlling during the synthesis the number of vacancies, provides an excellent opportunity to shift the MCE of such complexes.

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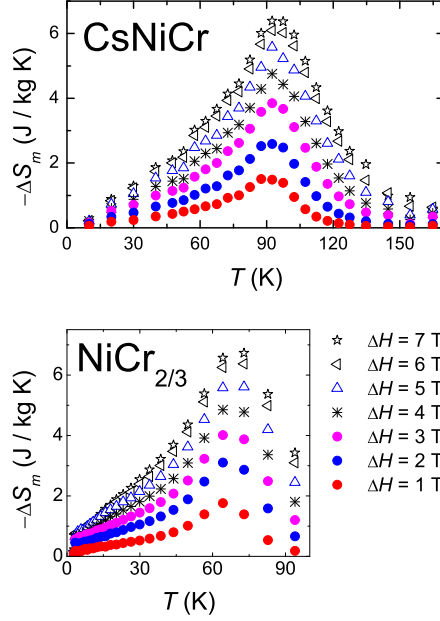


Fig. 4. Magnetic entropy change $\Delta S_m(T)$ as obtained from $M(T, H)$ data of Fig. 3 for CsNiCr (top) and NiCr_{2/3} (bottom), for several field changes ΔH , as labelled.

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